

tainty) and using our low temperature results (considering their experimental errors) we finally get  $E_1 = -(2.7 \pm 0.3)$  eV and  $E_2 = +(2.8 \pm 0.2)$  eV.

*Note added in proof.* It has been pointed out by Dr. S. H. Koenig that it is somewhat inappropriate to assume parabolic electron energy bands. Using more recent estimates of the total number of electrons  $N = 3 \times 10^{17}/\text{cm}^3$  at 4.2°K, he has suggested an effective parabolic Fermi energy for electrons to be 0.015 eV

such that expression (6) is validated. This gives an overlap energy  $E_0 = 0.027$  eV and consequently (within  $\pm 10\%$ )  $E_1 = -2.4$  eV and  $E_2 = +2.5$  eV.

#### ACKNOWLEDGMENTS

We should like to express our thanks to Dr. S. H. Koenig for helpful comments on our manuscript. We thank H. Weibel for valuable technical assistance during the course of this experiment.

## Hyperfine and Superhyperfine Structure of Manganese in $\text{SnO}_2$ †

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The electron paramagnetic resonance spectrum of manganese in a single crystal of  $\text{SnO}_2$  (cassiterite) was investigated at  $K$  and  $K_A$  band frequencies at a temperature of 77°K. The manganese atoms occupy  $\text{Sn}^{4+}$  substitutional sites giving the same charge with a resulting spin ground state of  $S = 3/2$ . The hyperfine structure (HFS) with  $I = 5/2$  and the superhyperfine structure (SHFS) show large anisotropies which can be explained by the relatively large values of  $D$  and  $E$  in the spin-Hamiltonian. The strong overlaps of the wave functions of the central manganese ion with those of the nearest-neighbor tins along the  $C$  axis accounts for the large SHFS,  $a = 34$  G. An attempt to explain these data from the experimental evidence is given. The spin-Hamiltonian and the constants for the  $C$  axis and magnetic  $Z$  axis coincident are

$$H = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} + \sum_{i=1}^2 \mathbf{S} \cdot \mathbf{a}_i \cdot \mathbf{I}_{Sn}$$

	$x[110]$	$y[110]$	$z[001]$	Tolerance
$g$	1.9879	1.9870	1.9907	$\pm 0.0003$
$A$ (gauss)	77.7	75.4	80.64	$\pm 0.5$
$a$ (gauss)	30.5	29.5	34.0	$\pm 0.5$
$D$ (kMc/sec)	26.436			$\pm 0.01$
$E$ (kMc/sec)	7.91			$\pm 0.01$

In addition, the resonance results obtained for  $\text{Mn}^{4+}$  in  $\text{SnO}_2$  are compared with those obtained for  $\text{Cr}^{3+}$  and  $\text{V}^{4+}$  in  $\text{SnO}_2$  and for  $\text{Cr}^{3+}$ ,  $\text{V}^{4+}$ , and  $\text{Mn}^{4+}$  in  $\text{TiO}_2$ .

#### INTRODUCTION

THE paramagnetic resonance spectrum of the ground state of  $\text{Mn}^{4+}$  in  $\text{SnO}_2$  has been investigated to determine the constants of the applicable spin-Hamiltonian and to compare the experimental results with those obtained for certain other impurities in  $\text{SnO}_2$  and in the rutile form of  $\text{TiO}_2$ .

$\text{SnO}_2$  is isomorphic to  $\text{TiO}_2$  which has the rutile structure and belongs to the  $D_{4h}^{14}$  space group.<sup>1</sup> The lattice parameters of  $\text{SnO}_2$  are  $a = 4.737$  Å,  $c = 3.185$  Å, and  $u = 0.307$  with  $c/a = 0.672$ .<sup>2</sup> The  $c$  axis<sup>2</sup> is the four-fold axis and it is chosen to be the  $Z$  magnetic axis. The values for  $\text{TiO}_2$  are  $a = 4.594$  Å,  $c = 2.959$  Å,  $u = 306$ , and  $c/a = 0.644$ .<sup>2</sup> There are two molecules of  $\text{SnO}_2$  in each unit cell.

† The SHFS as contained in this paper was discussed at the 25 June 1963 APS meeting held in Buffalo, New York.

\* The experimental data was obtained while one of us (WHF) was at Lincoln Laboratory, Lexington, Massachusetts.

<sup>1</sup> R. W. C. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1960).

<sup>2</sup> Werner H. Baur, *Acta Cryst.* **9**, 515 (1956).

The site symmetry of the Sn<sup>4+</sup> ions is  $D_{2h}$ . The manganese resonance data give an apparent local symmetry of  $D_{4h}$  which is due to the particular way the two nonequivalent sites transform into each other. These two sites, referred to as *A* and *B* sites, have the *x* axes along a  $[110]$  direction for the one and along the  $[\bar{1}10]$  direction for the other. As a consequence, when the magnetic field is along the *x* axis for the *A* sites, it is along the *y* axis for the *B* sites. The two sites are magnetically equivalent when the dc magnetic field lies in a (100) or (010) plane.

The unit cell of SnO<sub>2</sub> is shown in Fig. 1. The manganese ion which occupies the center of the unit cell is surrounded by 8 tins 3.708 Å away which are located at the corners of the unit cell. In addition, there are two tin ions along the crystal *c* axis which are 3.185 Å from the central manganese atom. Experimental evidence will be presented to show that these two tins which will be called "a" tins are responsible for the large superhyperfine structure which is observed.

The crystals used in these experiments were grown under the direction of T. Reed of the Lincoln Laboratory. Data concerning the techniques for growing these crystals are described elsewhere.<sup>3,4</sup> Spectrochemical analysis indicates that the manganese impurity replaced approximately 0.04% of the Sn ions and that other paramagnetic impurities existed in amounts two or three orders of magnitude less than that of Mn<sup>4+</sup>.

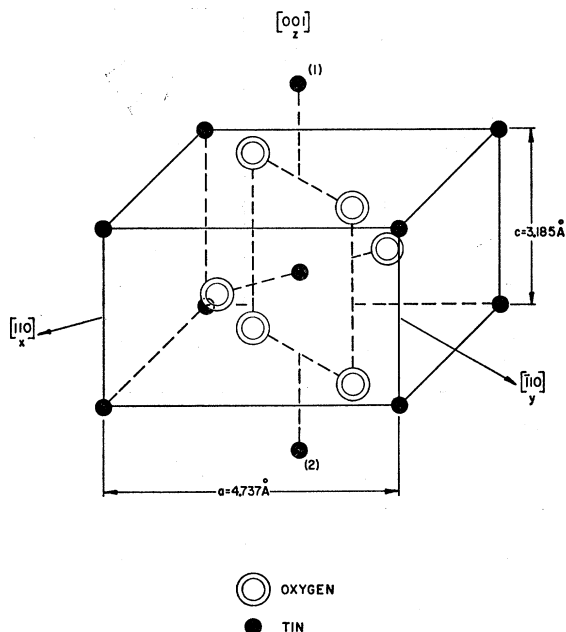


FIG. 1. Unit cell of cassiterite (SnO<sub>2</sub>).

<sup>3</sup> J. A. Marley and T. C. MacAvoy, *J. Appl. Phys.* **32**, 2504 (1961).

<sup>4</sup> T. B. Reed, J. T. Roddy, and A. N. Mariano, *J. Appl. Phys.* **33**, 1014 (1962).

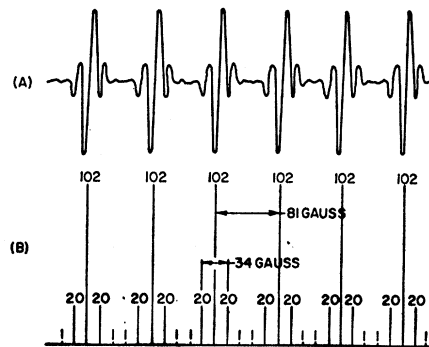


FIG. 2. Manganese resonance at 35 kMc/sec for  $\theta=0^\circ$  and  $\phi=0^\circ$  near 4500 G. The relative amplitudes of the SHFS to the HFS resonances and their strengths are given in (B).

### THEORY

The  $^4F$  ground state of the free ion of Mn<sup>4+</sup> is split into two triplets and a singlet when placed in a cubic octahedral environment. The orbital singlet lies lowest and is designated  $^4A_{2g}$ . This fourfold ground state is then split by a rhombic field as can be noted from the oxygen-tin distances along the different axes.

The spin-Hamiltonian which is used to describe the resonance data is<sup>5</sup>

$$\begin{aligned}
 H = & \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) \\
 & + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) \\
 & + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z + \sum_{i=1}^2 \mathbf{S} \cdot \mathbf{a}_i \cdot \mathbf{I}_{\text{Sn}}, \quad (1)
 \end{aligned}$$

where  $S$  is  $\frac{3}{2}$ ,  $I$  is  $\frac{5}{2}$ , and  $I_{\text{Sn}}$  is  $\frac{1}{2}$ . The last term in Eq. (1) represents the energy due to the SHFS arising from the two tins located along the *c* axis and flanking the manganese ion. Because the quadrupole resonance data was obscured by the strong SHFS, Eq. (1) does not include any quadrupole terms.

The SHFS term *a* is due mainly to the direct overlap of Sn-Mn orbitals. The odd isotopes of tin are Sn<sup>115</sup>, Sn<sup>117</sup>, and Sn<sup>119</sup>; their nuclear spin is  $\frac{1}{2}$ ; and their nuclear magnetic moments are all approximately one nuclear magneton. The natural abundance of the three isotopes treated collectively is 16%. A calculation of the relative amplitudes of the SHFS to be expected according to occupational probability and relative abundance of the odd isotopes of tins for the *a*-tins leads to the ratios 1:20:102:20:1. The magnitudes of the SHFS obtained from the experimental data and shown in Fig. 2 agree with the calculated ratios within experimental limits.

### EXPERIMENT

The resonance measurements were performed at 23.725 kMc/sec and at three frequencies in the  $K_A$  band.

<sup>5</sup> B. Bleaney and K. W. H. Stevens, *Reports on Progress in Physics* (The Physical Society, London, 1953), Vol. 16, p. 107.

The resonance data for 23.725 kMc/sec as a function of magnetic field and orientation is given in Fig. 3. The rotational resonance data in the  $K_A$  band was made at 35 kMc/sec, whereas subsequent measurements to check the resonance data along the three axes resulted in measurements being made at two other frequencies as noted on Fig. 4. The data in these figures represent the center of gravity of the hyperfine structure lines. Most of the measurements were made at liquid-nitrogen temperature. Some resonance measurements were also

made near 60 kMc/sec and resulted in a measured 59.6-kMc/sec zero-field splitting.

The secular determinant of the Hamiltonian was solved for the resonance energies along the three axes. The parameters were then adjusted until consistent results were obtained. A 7090 computer was used for this part of the work. The complete secular determinant, using second order terms in  $A$ , was then computed as a function of angle. The constants of the Hamiltonian as obtained by this process are given in Table I. The agreement between the experimental resonance data and that calculated is better than 10 mc/sec for both  $K$  and  $K_A$  bands. The calculated zero-field splitting is 59.55 kMc/sec. The rotational resonance data clearly checks with the assumption of a ground-state spin of  $\frac{3}{2}$  and has the symmetry of a substitutional site.

The rotational measurements made at 15-deg intervals between the major axes brought out the interesting strong anisotropy in both the HFS and SHFS. Figure 5

TABLE I. The spin-Hamiltonian parameters for  $Mn^{4+}$  in  $SnO_2$ .

	$x[110]$	$y[\bar{1}10]$	$z[001]$	Tolerance
$g$	1.9879	1.9870	1.9907	$\pm 0.0003$
$A$ (gauss)	77.7	75.4	80.64	$\pm 0.5$
$a$ (gauss)	30.5	29.5	34.0	$\pm 0.5$
$D$ (kMc/sec)	26.436			$\pm 0.01$
$E$ (kMc/sec)	7.91			$\pm 0.01$

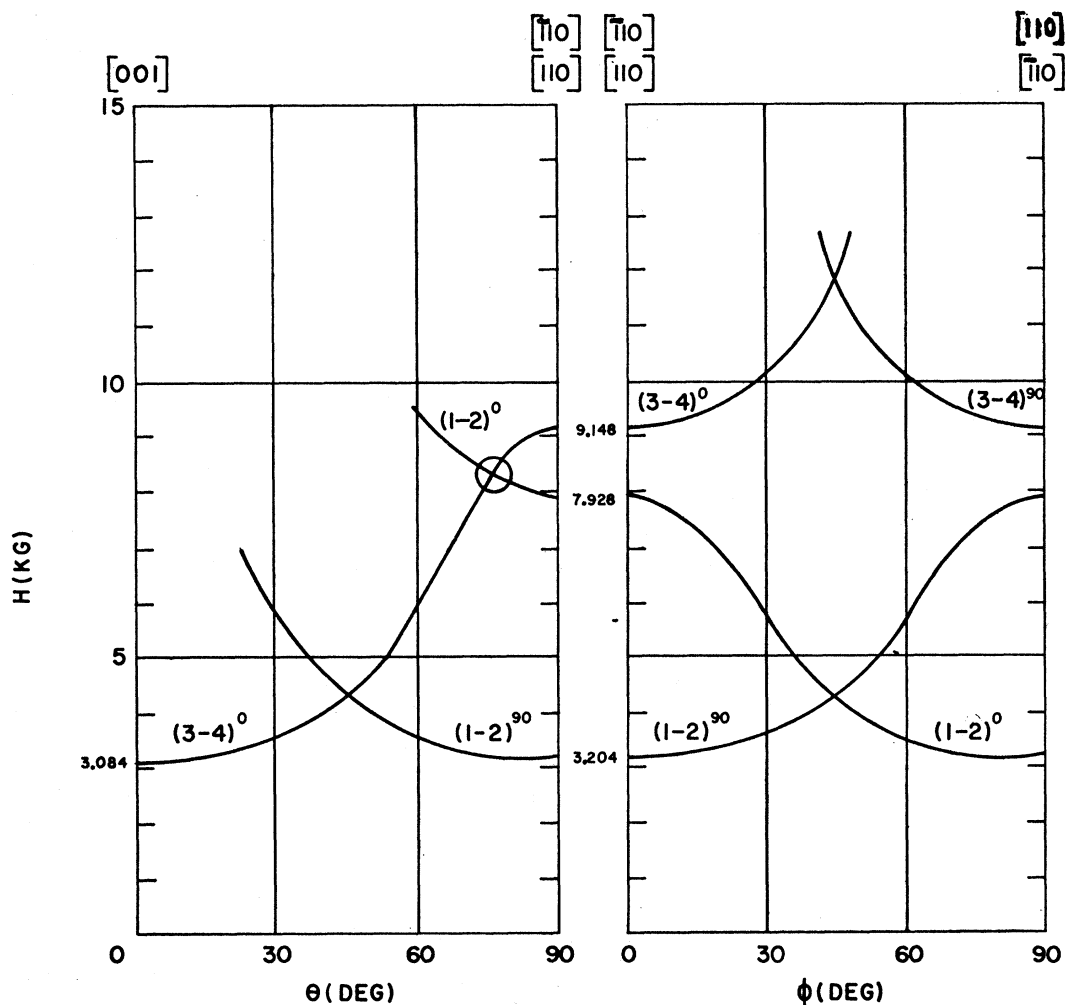


FIG. 3. Observed resonances of  $Mn^{4+}$  in  $SnO_2$  at 23.725 kMc/sec. The circle represents an orientation at which the 1-2 transition equals the 3-4 transition.

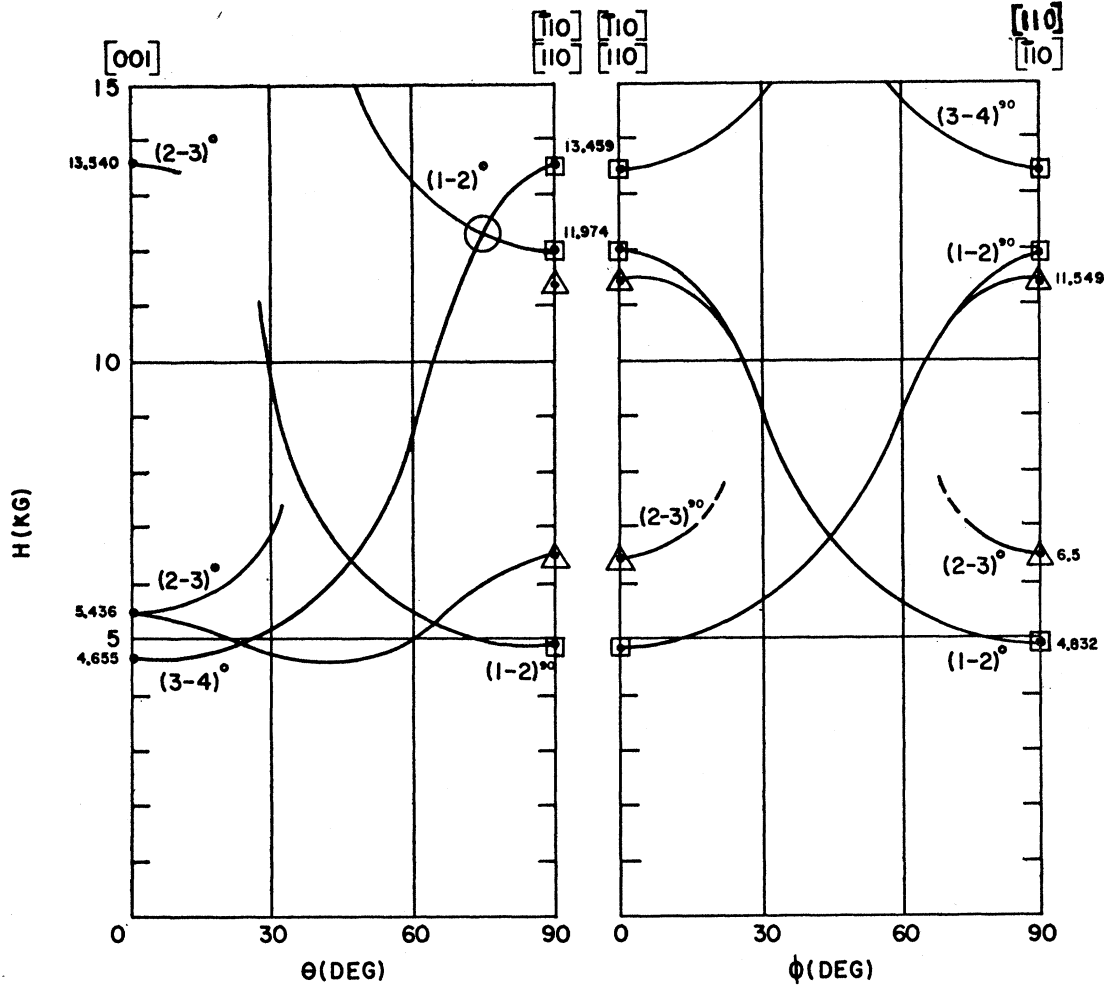


Fig. 4. Observed resonances of  $Mn^{4+}$  in  $SnO_2$  at Ka band. Magnetic fields measured at 35 475 are indicated by dots, those at 35 348 by  $\square$ , those at 34 990 by  $\Delta$ . The circle represents an orientation at which the 1-2 transition equals the 3-4 transition.

shows this experimentally determined data as a function of magnetic field orientation from the  $C$  axis to the  $[110]$  axis. The calculated data for the HFS are also shown. Similar results were obtained between the  $[110]$  and  $[\bar{1}10]$  directions but in this case there was symmetry about the  $[100]$  direction and the anisotropy was smaller. These anisotropies are due to the large zero-field splitting which is reflected in the values of  $D$  and  $E$  obtained.

The collapse of the hyperfine structure for the two central levels as shown in Fig. 6 corresponds to dc magnetic fields of approximately 6000 and 13 000 G. A calculation to determine the values of  $D$  and  $E$  for this to occur serves as a check of the parameters. The cross-over levels  $W_{4-3}$  and  $W_{2-1}$  as shown by the circles in Figs. 3 and 4 for the angle  $\theta = 77^\circ$  and  $\phi = 0^\circ$  is also consistent with the ratio of  $D/E$ . In addition, the zero-field splitting gave a check of the values of  $D$  and  $E$ . Thus, the calculated values for  $D$  and  $E$  and those obtained from the resonance data agree within experimental error.

#### DISCUSSION

A comparison of the experimental results obtained for  $Mn^{4+}$ ,  $Cr^{3+}$ , and  $V^{4+}$  in  $SnO_2$  and  $TiO_2$  is given in Table II.<sup>6-11</sup> The values obtained in the cases where another axial system is used have been transformed to the system of axes used in this report. This required changing only the results of the vanadium ion in the two host crystals.

It is interesting to note that only in the case of  $SnO_2$  is a large superhyperfine structure noted for  $V^{4+}$ ,  $Cr^{3+}$ , and  $Mn^{4+}$ . This is reasonable to expect since the SHFS is due to the nearest neighbor metal ions and in the case of  $TiO_2$  the titanium odd-isotopes have large nuclear

<sup>6</sup> W. H. From, Phys. Rev. **131**, 961 (1963).

<sup>7</sup> P. H. Kasai, Phys. Letters **7**, 5 (1963).

<sup>8</sup> W. From, C. Kikuchi, P. B. Dorain (unpublished).

<sup>9</sup> H. G. Andersen, J. Chem. Phys. **35**, 1090 (1961).

<sup>10</sup> H. J. Gerritsen, S. E. Harrison, H. R. Lewis, and J. P. Wittke, Phys. Rev. Letters **2**, 153 (1959).

<sup>11</sup> H. J. Gerritsen and H. R. Lewis, Phys. Rev. **119**, 1010 (1960).

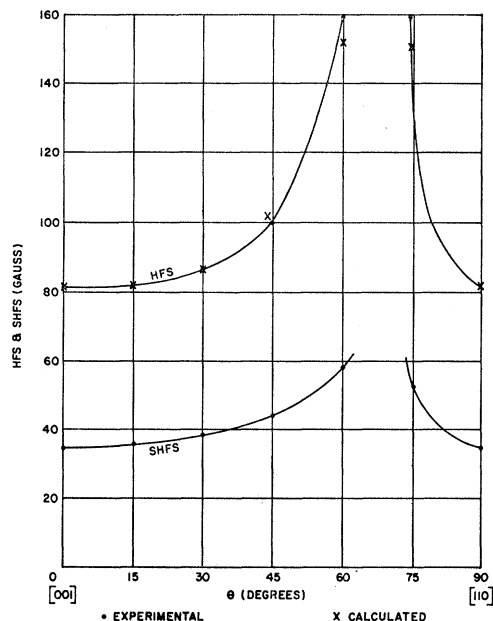


FIG. 5. The HFS and SHFS splitting as a function of the angle of the magnetic field and the (3-4) transition.

spins of  $\frac{5}{2}$  and  $\frac{7}{2}$  and relative abundance of approximately 8% and 5%, respectively. Possibly, electron-nuclear double resonance techniques will permit the determination of the SHFS of various paramagnetic ions in  $\text{TiO}_2$ .<sup>12</sup>

TABLE II. A comparison of the spin-Hamiltonian parameters for  $\text{Mn}^{4+}$ ,  $\text{Cr}^{3+}$ , and  $\text{V}^{4+}$  in  $\text{SnO}_2$  and  $\text{TiO}_2$ . The  $b$  term represents the superhyperfine interaction of the 4 tins in the  $Y$ - $Z$  plane with the central manganese ion. Using ordinary resonance techniques only the "a" tin interaction was observed for manganese.

Material and ion	$\text{Mn}^{4+}$	$\text{SnO}_2$ $\text{Cr}^{3+}$	$\text{V}^{4+}$	$\text{Mn}^{4+}$	$\text{TiO}_2$ $\text{Cr}^{3+}$	$\text{V}^{4+}$
$g_x$ [110]	1.9879	1.975	1.943	1.995	1.97	1.956
$g_y$ [110]	1.9870		1.939	1.991		1.915
$g_z$ [001]	1.9907		1.903	1.990		1.913
$A_x$ (gauss)	77.7	45 <sup>a</sup>	154.4	77.5	45	152.1
$A_y$	75.4		23.3	75.4		33.2
$A_z$	80.64		47.03	78		46.1
$a_x$ (gauss)	30.5	38	165.2			
$a_y$	29.5		166			
$a_z$	34		172.6			
$b_x$ (gauss)			28			
$b_y$			28			
$b_z$			28			
Zero-field splitting (kMc/sec)	59.55	45.3		28	43.3	
$D$ (kMc/sec)	26.436	17.3		12.23	16.5	
$E$ (kMc/sec)	7.91	8.4		3.92	8.1	
Reference	This paper	6	7 and 8	9	10	11

<sup>a</sup> Revised since date of Ref. 6.

<sup>12</sup> Recently, T. Chang has reported on  $\text{W}^{5+}$  in  $\text{TiO}_2$  [Bull. Am. Phys. Soc. 9, 568 (1964)] and on  $\text{W}^{6+}$  in  $\text{TiO}_2$  [Bull. Am. Phys. Soc. 8, 464 (1963)] in which superhyperfine interaction is observed.

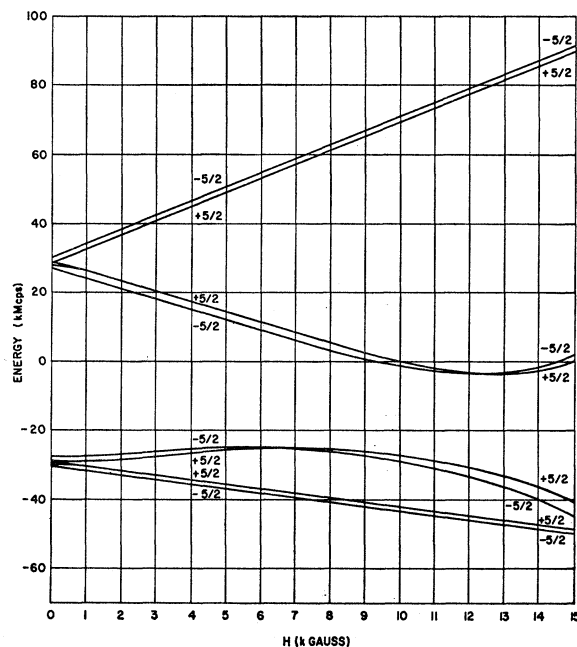


FIG. 6. Collapse of hyperfine structure lines near 6- and 12.5-kG  $M_1$  designations are noted at low and high fields.

A check at low temperature was made to determine the possible existence of  $\text{Mn}^{3+}$  in  $\text{SnO}_2$  which was found in  $\text{TiO}_2$ .<sup>13</sup> Since  $\text{TiO}_2$  exists in various forms, such as  $\text{Ti}_5\text{O}_9$ , finding  $\text{Mn}^{3+}$  in Rutile should not be too surprising; however, the results were negative for  $\text{SnO}_2$  probably because the  $\text{SnO}_2$  crystal investigated was apparently well behaved.

Also, in re-examining  $\text{Cr}^{3+}$  in  $\text{SnO}_2$ , several of the resonances which were seen but not explained, can now be attributed to interstitial  $\text{Cr}^{3+}$ . Neither in the case of  $\text{Mn}^{4+}$  or  $\text{V}^{4+}$  has such an interstitial position been observed. The resonance data shows a  $10^\circ$  to  $15^\circ$  rotation of the  $x$  and  $y$  axes which would correspond to an interstitial position.

The zero-field splittings of  $\text{Cr}^{3+}$  in  $\text{SnO}_2$  and in  $\text{TiO}_2$  are approximately identical. However, the zero field splitting of  $\text{Mn}^{4+}$  in  $\text{SnO}_2$  is slightly more than twice as large as that for  $\text{Mn}^{4+}$  in  $\text{TiO}_2$ . This is an unusual condition and at the present time we have no satisfactory explanation.

#### ACKNOWLEDGMENTS

The authors thank C. Work of Lincoln Laboratory for his important computer programming effort and A. Mariano of Kennecott Copper Research Laboratory for crystal analysis and orientation data.

<sup>13</sup> H. J. Gerritsen, and E. S. Sabisky, Phys. Rev. 132, 1507 (1963).